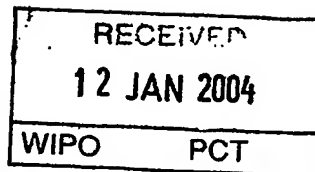


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**APPLICATION NUMBER: 60/455,508**

**FILING DATE: March 18, 2003**

**RELATED PCT APPLICATION NUMBER: PCT/US03/34597**



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03/18/03  
J1031 U.S. PTO

Assistant Commissioner for Patents  
Box PROVISIONAL PATENT APPLICATION  
Washington, D.C. 20231

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03-19-03

PATENT

Docket No.

P02062US1A  
(FIR.P346)

**Transmittal of Provisional Application Pursuant to 37 C.F.R. § 1.53(c)**

Application of Yuan-Yong Yan  
whose respective address(es) are: 613 Redfield Lane  
Copley, Ohio 44321  
For THE USE OF SULFUR CONTAINING INITIATORS FOR ANIONIC  
POLYMERIZATION OF MONOMERS

30979 U.S. PTO  
60/455508

03/18/03

Enclosed is a new provisional patent application. It includes 33 pages of text and \_\_\_\_\_ sheet(s) of drawings.

1. Enclosed is an application assignment to and a completed Assignment Recordation Cover Sheet.
2. X Enclosed is return receipt postcard.
3. X The USPTO is authorized to charge the fee pursuant to 37 C.F.R. § 1.16(k) (\$160.00) to Deposit Account No. 06-0925. Also, during the pendency of this application, please charge any fees incurred and credit any overpayments made to that same Deposit Account.
4. X Kindly address all correspondence relating to this application to the following address:

Chief Intellectual Property Counsel  
Bridgestone/Firestone, Inc.  
1200 Firestone Parkway  
Akron, OH 44317-0001

Registration Number	Telephone Number
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Date	
March 18, 2003	

Signature
<i>Donald J. Bobak</i>
Print Name
Donald J. Bobak

**Certificate of Express Mailing**

- X Under 37 C.F.R. § 1.10, I certify that this application is being deposited, on the date indicated below, with the United States Postal Service "Express Mail Post Office to Addressee" service addressed to the Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

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AppTr-Provisional (Oct-00)

Signature of Person Making Certification
<i>Cynthia M. Wilson</i>
Printed Name of Person Making Certification
Cynthia M. Wilson

EL726086762US

## THE USE OF SULFUR CONTAINING INITIATORS FOR ANIONIC POLYMERIZATION OF MONOMERS

### BACKGROUND OF THE INVENTION

5           Anionic polymerization is a well-known type of chain-reaction polymerization that typically employs either a base or an organometallic as a polymerization initiator. Exemplary organometallics that are well-known as anionic-polymerization initiators for diene monomers, with and without monovinyl aromatic monomers, include alkyl lithium, trialkyltin lithium, and certain aminolithium  
10       compounds. The synthesis of lithiodithiane reagents is known as is their addition to conjugated ketones. However, no use of sulfur containing initiators, particularly lithio thio aryl based compounds, is known for anionic polymerization.

          Anionic polymerization of diene monomers such as butadiene and isoprene, with and without monovinyl aromatics such as styrene, commonly yields  
15       elastomers that can be used in a variety of commercial applications; one such application involves employing the elastomers in constructing tires. Because of the great commercial demand for these types of elastomers, there is a need for anionic-polymerization initiators that can be employed for their synthesis.

          Synthesis of a polymer having a head group that will interact with the  
20       filler, used to reinforce many elastomeric compounds, and thereby reduce hysteresis is desirable.

### SUMMARY OF THE INVENTION

          In general, the present invention advances the art by providing new  
25       organometallic anionic polymerization initiators for polymerizing diene monomers.

          The present invention provides a method for anionically polymerizing monomers comprising the step of polymerizing the monomers with a sulfur containing anionic initiator to provide a functional head group on the polymer.

The present invention further provides a method for synthesizing a polymer comprising a headgroup functionality that can reduce the hysteresis of an elastomeric compound comprising both the polymer and a filler material.

5 Additionally, anionically polymerizing monomers, using lithio thio aryls as an initiator, yields polymers comprising a head group functionality that can react with fillers such as carbon black and silica.

The present invention further provides vulcanizable elastomeric compounds having a head group functionality that is reactable with reinforcing fillers having phenolic functionalities, thereby providing reduced hysteresis.

10 The present invention also provides pneumatic tires having at least one component manufactured from a vulcanizable elastomeric compound having a head group functionality that is reactable with reinforcing fillers having phenolic functionalities, thereby providing reduced hysteresis.

15 In general, the present invention provides a method for anionically polymerizing monomers comprising the step of polymerizing the monomers with a sulfur containing anionic initiator to provide a functional head group on the polymer.

The present invention also provides a method for anionically polymerizing monomers comprising the steps of synthesizing a sulfur containing anionic initiator *in situ* and polymerizing the monomers with the sulfur containing  
20 anionic initiator to provide a functional head group on the polymer.

The present invention also provides a vulcanizable elastomer having reduced hysteresis properties comprising a plurality of polymer molecules wherein substantially each polymer molecule contains a functional head group derived from a sulfur containing anionic initiator; and from about 20 to about 100 parts by weight of  
25 carbon black, per 100 parts of the elastomer.

The present invention also provides an improved tire having decreased rolling resistance resulting from a treadstock containing a vulcanizable elastomer compound comprising an elastomer comprising a plurality of polymer molecules wherein substantially each polymer molecule contains a functional head group

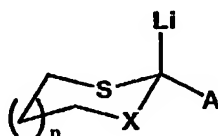
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derived from a sulfur containing anionic initiator; and from about 20 to about 100 parts by weight of carbon black, per 100 parts of the elastomer.

### DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

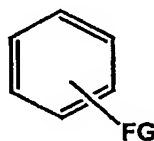
5           The present invention provides a method for anionically polymerizing monomers by employing lithio thio aryls as a polymerization initiator. Suitable lithio thio aryls have the general formula



10

where X is selected from the group consisting of S, O and NR<sub>4</sub>, where R is selected from the group consisting of trimethyl-, triethyl- and tripropyl-silyl groups, C<sub>1</sub> to C<sub>20</sub> alkyl groups, C<sub>4</sub> to C<sub>20</sub> cycloalkyl groups, C<sub>6</sub> to C<sub>20</sub> aryl group and mixtures thereof; where n = 0 to 3 and A is selected from the group consisting of phenyl, functionalized phenyls; thienyl, furyl, puridyl, naphthyl, binaphthyl, and pyrenyl; where the

15

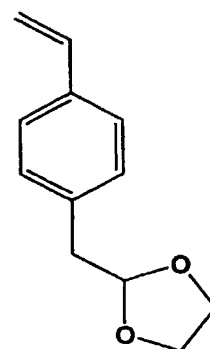
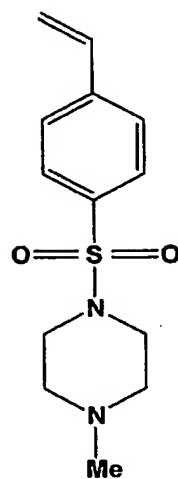
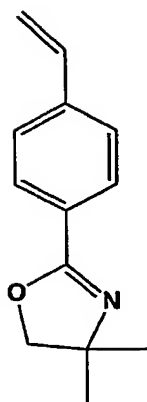
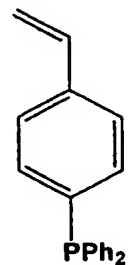
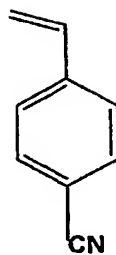
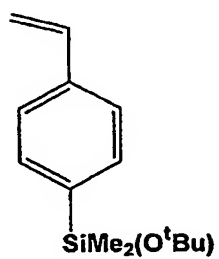


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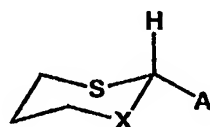
where FG is selected from the group consisting of C<sub>1</sub> to C<sub>10</sub> alkyl groups, C<sub>2</sub> to C<sub>10</sub> alkenyl groups, C<sub>3</sub> to C<sub>10</sub> alkynyl groups, ethers, *tert*-amines, oxazolines, phosphines, sulfides, silyls, monosaccharides, sterically hindered esters and mixtures thereof. Exemplary FG groups include the following:

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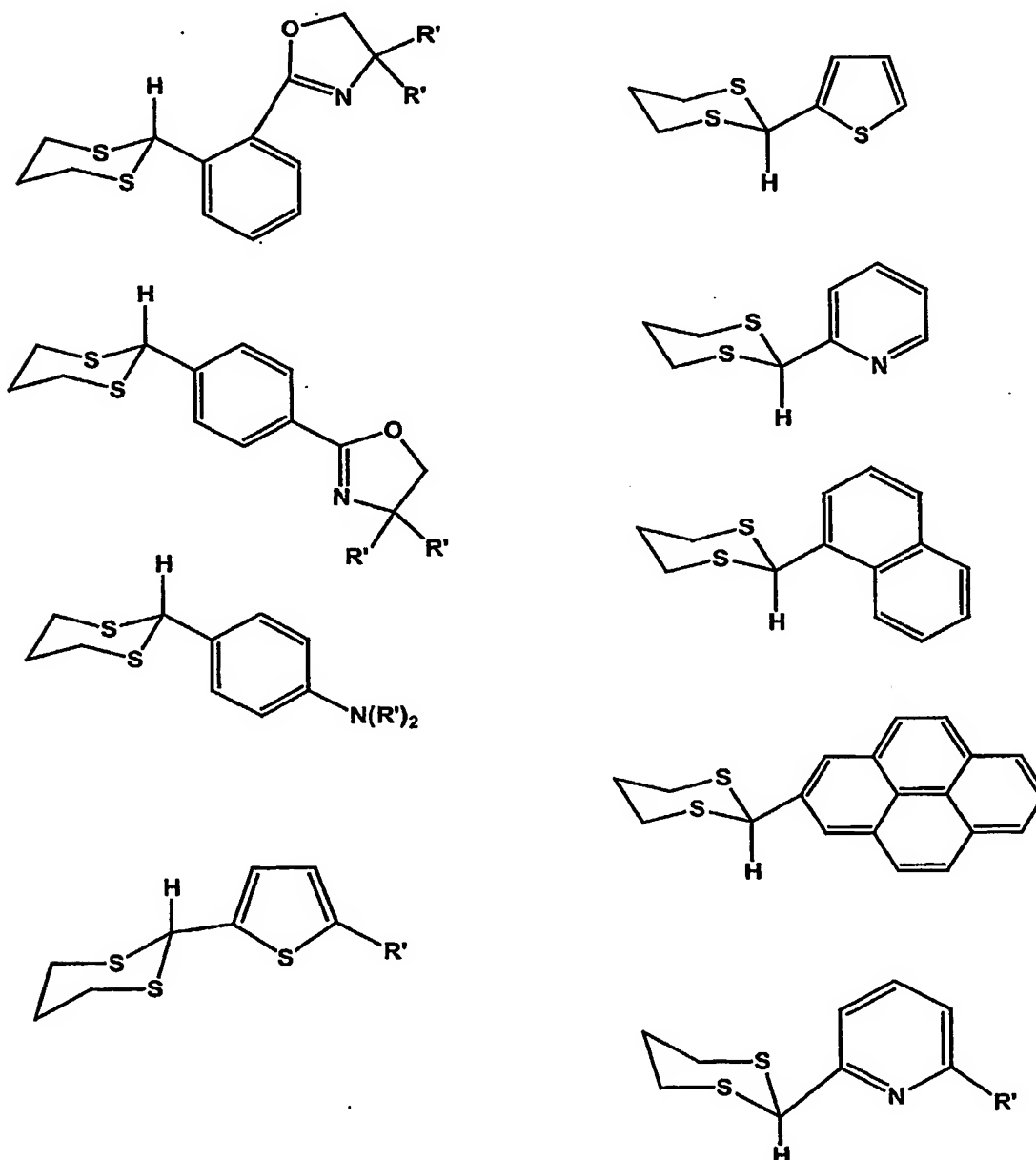
The initiators of the present invention are prepared either prior to use or *in situ* by reacting an initiator precursor with an organolithium compound e.g, butyllithium to form the initiator. Precursors have the formula



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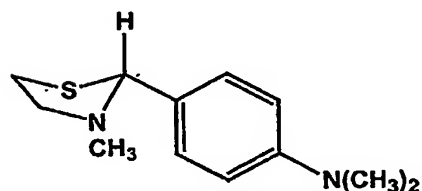
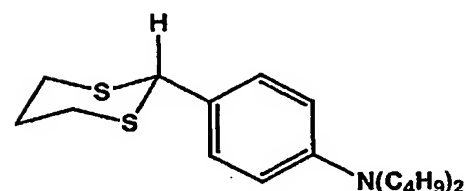
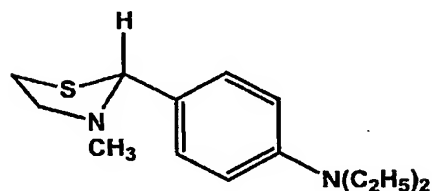
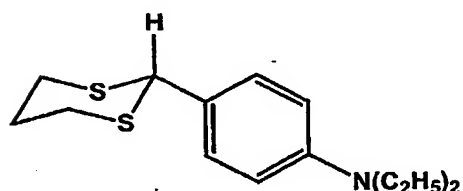
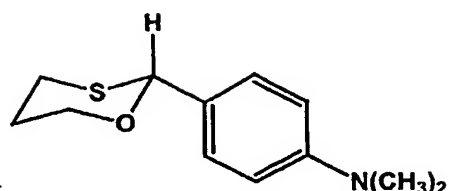
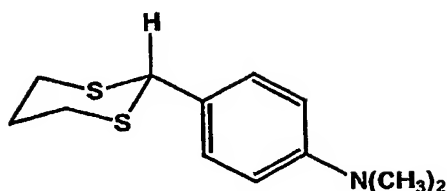
It is also preferable to employ functionalized precursors to prepare the initiators and several representative species are as follows:



5 where R' is H, C<sub>1</sub> to C<sub>10</sub> alkyl or C<sub>4</sub> to C<sub>20</sub> cycloalkyl.

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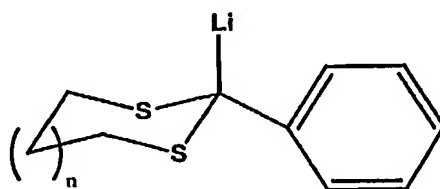
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For a comprehensive summary of known functionalized phenyls, see the article "Recent advance in living anionic polymerization of functionalized styrene derivatives", by Hirao et al, *Prog. Polym. Sci.* (2002) 1399-1471, Elsevier, the subject matter of which is incorporated herein by reference.

Polymerization can be initiated by contacting an initiator of the present invention with a solution comprising diene monomer. This can be achieved by either adding the initiator to a solution comprising diene monomer, or it can be achieved by synthesizing the initiator in a solution comprising diene monomer.

A preferred initiator is 2-lithio-2-phenyl-1,3-dithiane (PDT-Li). Its structure can be represented as follows, where  $n = 0$  to 3:





As stated above, 2-lithio-2-phenyl-1,3-dithiane is employed as an anionic polymerization initiator by contacting it with a solution comprising diene monomers. The solution is generally heated to about 24°C before the initiator is added thereto or synthesized therein. After the initiator contacts the solution, the reaction temperature is generally increased to about 54°C. Anionic polymerization of the diene monomer is generally complete after approximately 25 minutes.

The lithio thio aryls can be employed as an anionic polymerization initiator in amounts ranging from about 1 to about 1000 meq/kg of monomer. Preferably, they are employed in amounts ranging from about 3 to about 12 meq/kg of monomer. More preferably, the initiator is employed in an amount ranging from about 4 to about 8 meq/kg of monomer.

The initiator thus formed may be employed as an initiator to prepare any anionically-polymerized elastomer, e.g., polybutadiene, polyisoprene and the like, and copolymers thereof with monovinyl aromatics such as styrene, alpha methyl styrene and the like, or trienes such as myrcene. Thus, the elastomers include diene homopolymers and copolymers thereof with monovinyl aromatic polymers. Suitable monomers include conjugated dienes having from about 4 to about 12 carbon atoms and monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes. Examples of conjugated diene monomers and the like useful in the present invention include 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene and 1,3-hexadiene, and aromatic vinyl monomers include styrene,  $\alpha$ -methylstyrene, *p*-methylstyrene, vinyltoluene and vinylnaphthalene.

Non-limiting examples of useful polymers that can be synthesized by methods that employ an anionic polymerization initiator of the present invention include, but are not limited to polybutadiene, styrene-butadiene rubber, synthetic polyisoprene, butadiene-isoprene rubber, styrene-isoprene rubber, styrene-isoprene-butadiene rubber, and terminal and backbone functionalized derivatives thereof.

Polymerization is conducted in polar solvent, such as tetrahydrofuran (THF), or a hydrocarbon solvent, such as the various oligomers of hexanes, heptanes, octanes, pentanes, their alkylated derivatives, and mixtures thereof. When an initiator

is employed having a greater molecular weight, attributable to the size of functional groups that may be incorporated, the former are soluble in the more common and available solvents such as hexane and the like. In either instance, in order to promote randomization in copolymerization and to control vinyl content, a polar coordinator  
5 may be added to the polymerization ingredients. Amounts range between 0 and 90 or more equivalents per equivalent of lithium. The amount depends on the amount of vinyl desired, the level of styrene employed and the temperature of the polymerization, as well as the nature of the specific polar coordinator (modifier) employed. Suitable polymerization modifiers include for example, ethers, or amines  
10 to provide the desired microstructure and randomization of the comonomer units.

Other compounds useful as polar coordinators include tetrahydrofuran (THF), linear and cyclic oligomeric oxolanyl alkanes such as 2,2-bis(2'-tetrahydrofuryl) propane, di-piperidyl ethane, di-piperidyl methane, hexamethylphosphoramide, N-N'-dimethylpiperazine, diazabicyclooctane, dimethyl  
15 ether, diethyl ether, tributylamine and the like. The linear and cyclic oligomeric oxolanyl alkane modifiers are described in U.S. Pat. No. 4,429,091, owned by the Assignee of record, the subject matter of which relating to such modifiers is incorporated herein by reference. Compounds useful as polar coordinators include those having an oxygen or nitrogen hetero-atom and a non-bonded pair of electrons.  
20 Other examples include dialkyl ethers of mono and oligo alkylene glycols; "crown" ethers; tertiary amines such as tetramethylethylene diamine (TMEDA); linear THF oligomers; and the like.

A batch polymerization is begun by charging a blend of monomer(s) and hydrocarbon solvents to a suitable reaction vessel, followed by the addition of the  
25 polar coordinator (if employed) and the initiator compound previously described. The reactants are heated to a temperature of from about 20° to about 200° C, and the polymerization is allowed to proceed for from about 0.1 to about 24 hours.

To terminate the polymerization, and thus further control polymer molecular weight, a terminating agent, coupling agent or linking agent may be  
30 employed, all of these agents being collectively referred to herein as "terminating

reagents". Certain of these reagents may provide the resulting polymer with a multifunctionality. That is, the polymers initiated according to the present invention, may carry the functional head group as discussed hereinabove, and may also carry a second functional group selected from the group consisting of terminating reagents, coupling agents and linking agents.

Useful terminating reagents are disclosed in U.S. Pat. Nos. 5,502,131, 5,496,940 and 4,616,069, the subject matters of which are incorporated herein by reference. They include the following compounds providing terminal functionality (e.g., "endcapping"): tin tetrachloride,  $(R)_3SnCl$ ,  $(R)_2SnCl_2$ ,  $RSnCl_3$ , carbodiimides, N-cyclic amides, N,N' disubstituted cyclic ureas, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino) benzophenone, and the like. Tin tetrachloride is preferred. The organic moiety R is selected from the group consisting of alkyls having from about 1 to about 20 carbon atoms, cycloalkyls having from about 3 to about 20 carbon atoms, aryls having from about 6 to about 20 carbon atoms and aralkyls having from about 7 to about 20 carbon atoms. Typical alkyls include n-butyl, s-butyl, methyl, ethyl, isopropyl and the like. The cycloalkyls include cyclohexyl, menthyl and the like. The aryl and the aralkyl groups include phenyl, benzyl and the like. Preferred endcapping agents are selected from the group consisting of tin tetrachloride, tributyl tin chloride, dibutyl tin dichloride and 1,3-dimethyl-2-imidazolidinone.

While terminating to provide a functional group on the terminal end of the polymer is preferred, it is further preferred to terminate by a coupling reaction, with for example, tin tetrachloride or other coupling agent such as silicon tetrachloride ( $SiCl_4$ ), esters and the like.

When vulcanizable polymers, such as styrene-butadiene rubber (SBR) have been initiated according to the present invention and are then further terminated with a functional group Y, they contain a functional headgroup X and functional endgroup Y, which can be represented as X-Y Polymers.

2-lithio-2-phenyl-1,3-dithiane is a well-known composition that can be synthesized by persons having ordinary skill in the art by using conventional techniques. A non-limiting example of a method for preparing 2-lithio-2-methyl-1,3-dithiane involves adding 2-phenyl-1,3-dithiane to dried tetrahydrofuran and cooling to -78°C. A solution comprising butyllithium and hexane is then added thereto. The resulting solution is then stirred for approximately 3 hours and allowed to stand overnight at -25°C.

In an alternate embodiment, 2-lithio-2-phenyl-1,3-dithiane can be synthesized *in situ* in a solution comprising the monomer or monomers to be polymerized. A non-limiting example for performing this synthesis involves creating a solution comprising hexane, styrene monomer, and butadiene. This first solution is generally heated to about 24°C when 2-phenyl-1,3-dithiane and butyllithium are added thereto. The solution is then heated to approximately 54°C and allowed to react for approximately 40 minutes. More generally, the *in situ* preparation of anionic initiator is practiced by creating a solution comprising hexane, and the monomer(s) to be polymerized. This first solution is generally heated to about 24°C when the non-lithiated initiator precursor and butyllithium are added thereto. The solution is then heated to approximately 54°C and allowed to react for approximately 40 minutes, or comparable conditions necessary to allow the precursor and butyllithium to react.

The anionic polymers produced herein have functional headgroups, derived from the initiators of the present invention, which interact with conventional fillers used in the formulation of vulcanizable elastomeric (rubber) compounds. Typically, such fillers include silica or carbon black. The polymers can be compounded with silica in amounts ranging from about 5 to about 100 parts by weight, per 100 parts of rubber (phr), with about 10 to about 90 phr being preferred.

The polymers can be compounded with carbon black in amounts ranging from about 20 to about 100 parts by weight, per 100 parts of rubber (phr), with about 40 to about 70 phr being preferred. The carbon blacks may include any of the commonly available, commercially-produced carbon blacks but those having a surface area (EMSA) of at least 20 m<sup>2</sup>/g and more preferably at least 35 m<sup>2</sup>/g up to 200 m<sup>2</sup>/g or higher are

preferred. Surface area values used in this application are those determined by ASTM test D-1765 using the cetyltrimethyl-ammonium bromide (CTAB) technique. Among the useful carbon blacks are furnace black, channel blacks and lamp blacks. More specifically, examples of the carbon blacks include super abrasion furnace (SAF) blacks, high abrasion furnace (HAF) blacks, fast extrusion furnace (FEF) blacks, fine furnace (FF) blacks, intermediate super abrasion furnace (ISAF) blacks, semi-reinforcing furnace (SRF) blacks, medium processing channel blacks, hard processing channel blacks and conducting channel blacks. Other carbon blacks which may be utilized include acetylene blacks. Mixtures of two or more of the above blacks can be used in preparing the carbon black products of the invention. Typical values for surface areas of usable carbon blacks are summarized in the following Table I.

TABLE I  
Carbon Blacks

	ASTM Designation (D-1765-82a)	Surface Area (m <sup>2</sup> /g) (D-3765)
15	N-110	126
	N-220	111
	N-339	95
20	N-330	83
	N-550	42
	N-660	35

The carbon blacks utilized in the preparation of the rubber compounds of the invention may be in pelletized form or an unpelletized flocculant mass. Preferably, for more uniform mixing, unpelletized carbon black is preferred. The reinforced rubber compounds can be cured in a conventional manner with known vulcanizing agents at about 0.5 to about 4 phr. For example, sulfur or peroxide-based curing systems may be employed. For a general disclosure of suitable vulcanizing agents one can refer to Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., Wiley Interscience, N.Y. 1982,

Vol. 20, pp. 365-468, particularly "Vulcanization Agents and Auxiliary Materials" pp. 390-402. Vulcanizing agents may be used alone or in combination.

5 Vulcanizable elastomeric compositions of the invention can be prepared by compounding or mixing the polymers thereof with carbon black and other conventional rubber additives such as fillers, plasticizers, antioxidants, curing agents and the like, using standard rubber mixing equipment and procedures and conventional amounts of such additives. Such elastomeric compounds when vulcanized using conventional rubber vulcanization conditions have reduced hysteresis properties and are particularly adapted for use as tread rubbers for tires having reduced rolling resistance.

10

### General Experimental

In order to demonstrate practice of the present invention, the following examples have been prepared and tested. A dried 28 oz (795 cc) or 7 oz (199 cc) glass bottle, which previously had been sealed with extracted septum liners and perforated crown caps under a positive nitrogen purge, was used for all of the preparations. Butadiene in hexane (21.9 weight percent butadiene), styrene in hexane (styrene blend, 33 weight percent styrene), hexane, n-butyllithium (1.68 M in hexane), cyclic oligomeric oxolanyl alkane modifier in hexane (1.6 M solution in hexane, stored over calcium hydride), and BHT solution in hexane were used as supplied. Tetrahydrofuran (THF) was distilled from potassium benzophenone ketyl. Commercially available reagents and starting materials (Aldrich Chem. Co.) include the following: 2-phenyl-1, 3-dithiane, benzaldehyde dimethyl acetal, 1,3-propanedithiol, and 3-mercapto-1-propanol, which were used as purchased without further purification. The examples should not, however, be viewed as limiting the scope of the invention. The claims will serve to define the invention.

25

**EXAMPLES****Example No. 1****Synthesis of 2-lithio-2-phenyl-1,3-dithiane**

To a solution of 2-phenyl-1, 3-dithiane (2.1 g, 10.69 mmol) in THF (5 ml) and cyclohexane (10 ml) was added n-BuLi (6.37 ml, 1.68 M in hexane) dropwise via a syringe at -78° C. The solution was stirred for an additional 3 hours at 0° C. The resulting 2-lithio-2-phenyl-1, 3-dithiane (abbreviated as PDT-Li) was used for anionic initiator for polymerizing butadiene and/or butadiene/styrene and stored in an inert atmosphere of nitrogen at a refrigerator.

10

**Example No. 2**

To a solution of 2-phenyl-1, 3-oxathiane (1.0 g, 5.5 mmol) in THF (5.8 ml) and hexane (5 ml) was added n-BuLi (3.3 ml, 1.68 M in hexane) dropwise via a syringe at -78° C. The solution was stirred for an additional 3 hours at -5° C. The resulting 2-lithio-2-phenyl-1, 3-oxathiane (abbreviated as POT-Li) was used as anionic initiator for polymerizing butadiene and/or butadiene/styrene.

15

**Example No. 3**

A bottle was charged with 163.6 g of hexane, and 136.4 g of butadiene, then 0.55 ml of PDT-Li (Ex. No. 1) by syringe. The bottle was agitated and heated at 50° C for 1.5 hours. The polymer cement was terminated with a small amount of 2-propanol, treated with 4 ml of BHT solution; worked up with 2-propanol, and dried under vacuum for 12 hours.

20

**Example No. 4**

The preparation and the procedure used in Example 3 were repeated, but use of POT-Li (Ex. No. 2) as initiator. All polymers were analyzed by GPC with using styrene as the standard and in THF solution. The molecular weights of the polymers are listed hereinbelow. It should be noted that the same initiator was used for Examples 3 and 3X and that the molecular weights of the resulting polymers differed. The same is true for Examples 4 and 4X and their initiator.

Ex. No.	3	3X	4	4X
Initiator	PDT-Li	PDT-Li	POT-Li	POT-Li
Mn	60,940	120,620	99,410	126,910
Mw/Mn	1.07	1.05	1.08	1.16

All polymers were confirmed by UV trace.

**Example No. 5**

A bottle was charged with 190 g of hexane, 20 g of styrene blend, and 120 g of butadiene blend, then 0.61 ml of PDT-Li (Ex. No. 1) by syringe. The bottle was agitated and heated at 50° C for 1.5 hours. The polymer cement was terminated with a small amount of 2-propanol, treated with 4 ml of BHT solution, worked up with 2-propanol, and drum dried. Mn = 135,830, Mw/Mn = 1.11, Tg (°C), -69.

**Example No. 6**

A bottle was charged with 162.4 g of hexane, 137.6 g of butadiene, and 0.075 g of 2-phenyl-1, 3-dithiane, then 0.23 ml of n-BuLi (1.68 M in hexane) by syringe. The bottle was agitated and heated at 50° C for 1.5 hours. The polymer cement was terminated with a small amount of 2-propanol, treated with 4 ml of BHT solution; worked up with 2-propanol, and dried under vacuum for 12 hours. Polymer formation was confirmed by UV trace.



**Example No. 7**

The preparation and the procedure used in Example 6 were repeated, but without adding 2-phenyl-1, 3-dithiane. The product was a conventional polybutadiene and polymer formation was confirmed by UV trace.

5

**Example No. 8**

To a solution of 2-(4-dimethylamino)phenyl-1, 3-dithiane (1.25 g, 5.22 mmol) in THF (8 ml) and Et<sub>3</sub>N (1 ml) was added n-BuLi (3.1 ml, 1.68 M in hexane) dropwise via a syringe at -78° C. The solution was stirred for an additional 4 hours at 0° C. The resulting 2-lithio-2-(4-dimethylamino)phenyl-1, 3-dithiane (abbreviated as DAPDT-Li) was used as anionic initiator for polymerizing butadiene and/or butadiene/styrene and stored in an inert atmosphere of nitrogen at a refrigerator.

10

**Example No. 9**

A bottle was charged with 180 g of hexane, and 152 g of butadiene, then 1.6 ml of DAPDT-Li by syringe. The bottle was agitated and heated at 50° C for 1.5 hours. The polymer cement was terminated with a small amount of 2-propanol, treated with 5 ml of BHT solution; worked up with 2-propanol, and dried under vacuum for 12 hours.

15

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**Example No. 10**

The preparation and the procedure used in Example No. 9 were repeated, but using 1.0 ml of DAPDT-Li. All polymers were analyzed by GPC with using styrene as the standard and in THF solution. The molecular weights of the polymers are listed hereinbelow.

Example No.	9	10
Initiator	DAPDT-Li	DAPDT-Li
Mn	52,980	96,260
Mw/Mn	1.028	1.033

All polymers were confirmed by UV trace.

**Example No. 11**

A bottle was charged with 188 g of hexane, 20.18 g of styrene blend (32.7%), and 122 g of butadiene, then 1.0 ml of DAPDT-Li and 0.05 ml of cyclic oligomeric oxolanyl alkane modifier (1.6 M in hexane) by syringe. The bottle was agitated and heated at 50° C for 1.5 hours. The polymer cement was terminated with a small amount of 2-propanol, treated with 5 ml of BHT solution, work up with 2-propanol, and drum dried. Mn = 107,370, Mw/Mn = 1.11, Tg: -37.39° C.

**Example No. 12**

A bottle was charged with 188 g of hexane, 20.18 g of styrene blend (32.7%), and 122 g of butadiene (blend B-36), then 1.0 ml of DAPDT-Li by syringe. The bottle was agitated and heated at 50° C for 1.5 hours. The polymer cement was terminated with a small amount of 2-propanol, treated with 5 ml of BHT solution, work up with 2-propanol, and drum dried. Mn = 115,200, Mw/Mn = 1.087, Tg: -51.08° C.

**Example No. 13**

Into a two gallon (7.6 liter) N<sub>2</sub> purged reactor, equipped with a stirrer, was added 1.619 kg of hexane, 0.414 kg of 33 wt% styrene in hexane, and 2.451 kg of 22.2 wt% butadiene in hexane. The reactor was charged with 21 ml of 0.3 M of 2-lithio-2-(4-dimethylamino)phenyl-1, 3-dithiane (abbreviated as DAPDT-Li) and 1.05 ml of cyclic oligomeric oxolanyl alkane modifier (1.6 M in hexane) and then heated to 24° C. The reactor jacket was then heated to 50° C. After 16 minutes, the batch temperature peaked at 66.7° C. After an additional 25 minutes, the cement was removed from the reactor into dried 28-oz (795 cc) glass bottles, terminated with tributyltin chloride (3.68 M, abbreviated as DAPDT-SBR-SnBu<sub>3</sub>), 1,3-dimethyl-2-imidazolidinone (DMI, 9.14 M, abbreviated as DAPDT-SBR-DMI), and isopropanol (abbreviated as DAPDT-SBR-H) at 50° C bath for 30 minutes, respectively, coagulated in isopropanol containing butylated hydroxy toluene (BHT), and drum dried to yield the polymers with following properties:

DAPDT-SBR-H: Mn = 110,000 g/mol, Mw = 122,000 g/mol, Tg = -36.8° C; DAPDT-SBR-DMI: Mn = 66,000 g/mol, Mw = 84,900 g/mol, Tg = -37.0° C; and DAPDT-SBR-SnBu<sub>3</sub>: Mn = 110,000 g/mol, Mw = 120,000 g/mol, Tg = -36.8° C.

**Example No. 14**

The foregoing polymer was also prepared *in situ* as follows. To two gallons (7.6 liter) N<sub>2</sub> purged reactor equipped with a stirrer was added 1.610 kg of hexane, 0.412 kg of 33 weight percent styrene in hexane, and 2.462 kg of 22.1 weight percent butadiene in hexane. The reactor was then charged a mixture of 1.36 g of 2-(4-dimethylamino)phenyl-1-3dithiane in 10 ml of THF and 1 ml of triethylamine with 3.37 ml of n-BuLi (1.68 M) in hexane, and agitated at 24° C for 5 to 10 minutes, then 1.5 ml of cyclic oligomeric oxolanyl modifies (1.6 M OOPS in hexane) was charged, and the reactor jacket was then heated to 50° C. After 16 minutes, the batch temperature peaked at 62.9° C. After an additional 15 minutes, the cement was removed from the reactor into the dried 28 oz (795 cc) glass bottles, terminated with 1,3-dimethyl-2-imidazolidinone (DMI, 9.14 M, abbreviated as DAPDT-SBR-DMI), and

isopropanol (abbreviated as DAPDT-SBR-H) at 50° C bath for 30 minutes, respectively, coagulated in isopropanol containing butylated hydroxy toluene (BHT), and drum dried to yield the polymers with the following properties:

DAPDT-SBR-H:  $M_n = 123,000$  g/mol,  $M_w = 135,000$  g/mol,  $T_g = -34.3^\circ$  C.

- 5 DAPDT-SBR-DMI:  $M_n = 83,000$  g/mol,  $M_w = 94,000$  g/mol,  $T_g = -34.7^\circ$  C.

- The SBR polymer prepared according to Example No. 11 was utilized to prepare a vulcanizable elastomer, designated Stock A. For comparison, a control polymer was prepared using n-butyllithium as the initiator, designated Control Stock
- 10 A. Both stocks contained carbon black as the reinforcing filler and the formulations are provided in Table II. Amounts listed are presented by parts per hundred rubber (phr).

TABLE II  
CARBON BLACK FORMULATION

	Control Stock A	Stock A
Masterbatch		
Ingredient:		
n-BuLi – Initiator	100	
DAPDT-Li – Initiator		100
Carbon Black	55	55
Wax	1	1
Antiozonant	0.95	0.95
ZnO	2.5	2.5
Stearic Acid	2	2
Processing Oil	<u>10</u>	<u>10</u>
<b>Subtotal, Masterbatch (phr)</b>	<b>171.45</b>	<b>171.45</b>
FINAL		
Ingredient:		
Control Stock A	171.45	
Stock A		171.45
Sulfur	1.3	1.3
Accelerator, CBS	1.7	1.7
Accelerator, DPG	<u>0.2</u>	<u>0.2</u>
<b>Total (phr)</b>	<b>174.65</b>	<b>174.65</b>

The two polymers of Table II were next cured and then subjected to physical testing,  
 5 as set forth in Table III hereinbelow.

TABLE III  
DAPDT-SBR Compound Results  
**Carbon Black Formulations**

	Control Stock A	Stock A
Initiator:	n-BuLi	DAPDT-Li
Terminator:	IPA	IPA
Mn:	101,638	107,371
Mw/Mn:	1.05	1.11
ML <sub>1+4</sub> @ 100° C:		
T <sub>g</sub> (°C):	-41.2	-37.4
171° C MDR t <sub>50</sub> (min):	3.02	2.92
171° C MH-ML (Kg-cm):	16.9	20.9
ML <sub>1+4</sub> @ 130° C:	21.8	27.1
300% Modulus @ 23° C (MPa):	9.08	11.69
Tensile Strength @ 23° C (MPa):	15.73	16.17
Temp Sweep 0° C tan δ:	0.1688	0.1790
Temp Sweep 50° C tan δ:	0.2831	0.2355
RDA 0.25-14% ΔG' (MPa):	4.8917	4.2280
50° C RDA Strain sweep (5% strain) tan δ:	0.2620	0.2108
Bond Rubber (%):	1.1	19.0

- 5                   The SBR polymer prepared according to Example No. 11 was utilized to prepare a vulcanizable elastomer with a combination of carbon black and silica as fillers, designated Stock B. For comparison, a control polymer was prepared using n-butyl lithium as the initiator, also with a combination of carbon black and silica as fillers, designated Control Stock B. The complete formulations are provided in Table
- 10   IV. Amounts listed are presented by parts per hundred rubber (phr).

TABLE IV  
Silica/Carbon Black Formulation

Masterbatch	Control Stock B	Stock B
Ingredient:		
n-BuLi - Initiator	100	
DAPDT-Li - Initiator		100
Silica	30	30
Carbon Black	35	35
Wax	0	0
Antiozonant	0.95	0.95
Stearic Acid	1.5	1.5
LVA Oil	<u>10</u>	<u>10</u>
<b>Subtotal, Masterbatch (phr)</b>	<b>177.45</b>	<b>177.45</b>
Remill 1:		
Control Stock B	177.45	
Stock B		177.45
60% Si75 on 22.5% wax + 17.5% binder	<u>4.57</u>	<u>4.57</u>
<b>Total (phr)</b>	<b>182.02</b>	<b>182.02</b>

The two polymers of Table IV were next cured and then subjected to physical testing, as set forth in Table V hereinbelow.

TABLE V

## DAPDT-SBR Compound Results

**Silica/Carbon Black Formulations**

	Control Stock B	Stock B
Initiator:	n-BuLi	DAPDT-Li
Terminator:	IPA	IPA
Mn:	101,638	107,371
Mw/Mn:	1.05	1.11
171° C MDR $t_{50}$ (min):	8.37	6.49
171° C MH-ML (Kg-cm):	23.00	26.27
ML <sub>1+4</sub> @ 130° C:	60.2	78.1
300% Modulus @ 23° C (MPa):	7.1	9.8
Tensile Strength @ 23° C (MPa):	10.3	14.3
Temp Sweep 0° C tan $\delta$ :	0.1518	0.1572
Temp Sweep 50° C tan $\delta$ :	0.2431	0.2190
RDA 0.25-14% $\Delta G'$ (MPa):	6.570	7.436
50° C RDA Strain sweep (5% strain) tan $\delta$ :	0.2707	0.2341
Bond Rubber (%):	18.4	26.5

Considering the data in Table III, formulating a carbon black reinforced SBR polymer with the initiator DAPDT-Li provided a 19.5% reduction in tan  $\delta$ , compared to the polymer prepared with n-BuLi. Then, considering the data in Table V, formulating a silica/carbon black reinforced SBR polymer with the initiator DAPDT-Li provided a 13.5% reduction in tan  $\delta$ , compared to the polymer prepared with n-BuLi.

Based upon the foregoing disclosure, it should now be apparent that the use of the anionic polymerization initiators described herein provides a useful method



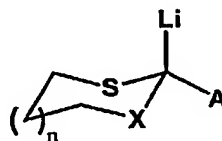
for the polymerization of diene monomers. It is, therefore, to be understood that any variations evident fall within the scope of the claimed invention and thus, the selection of specific component elements can be determined without departing from the spirit of the invention herein disclosed and described. In particular, anionic  
5 polymerization initiators according to the present invention are not necessarily limited to those dithianes exemplified herein.

Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth hereinabove. Thus,  
10 the scope of the invention shall include all modifications and variations that may fall within the scope of the attached claims.

## CLAIMS

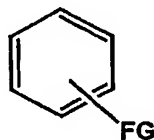
What is claimed is:

1. A method for anionically polymerizing monomers comprising the step of:  
 5 polymerizing said monomers with a sulfur containing anionic initiator to provide a functional head group on the polymer.
2. The method of claim 1, wherein said sulfur containing anionic initiator is a lithio thio aryl having the general formula



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where X is selected from the group consisting of S, O and NR<sub>4</sub>, where R is selected from the group consisting of trimethyl-, triethyl- and tripropyl-silyl groups, C<sub>1</sub> to C<sub>20</sub> alkyl groups, C<sub>4</sub> to C<sub>20</sub> cycloalkyl groups, C<sub>6</sub> to C<sub>20</sub> aryl group and mixtures thereof; where n = 0 to 3 and A is selected from the group  
 15 consisting of phenyl, functionalized phenyls; thienyl, furyl, puridyl, naphthyl, binaphthyl, and pyrenyl; where the functionalized phenyls have the formula

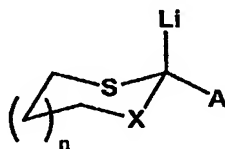


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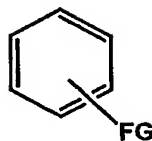
where FG is selected from the group consisting of C<sub>1</sub> to C<sub>10</sub> alkyl groups, C<sub>2</sub> to C<sub>10</sub> alkenyl groups, C<sub>3</sub> to C<sub>10</sub> alkynyl groups, ethers, *tert*-amines, oxazolines, phosphines, sulfides, silyls, monosaccharides, sterically hindered esters and mixtures thereof.

3. The method of claim 2, wherein said lithio thio aryl initiator is 2-lithio-2-phenyl-1,3-dithiane.
4. The method of claim 1, wherein said monomers are selected from the group consisting of conjugated dienes having from about 4 to about 12 carbon atoms and monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes and mixtures thereof.
5. The method of claim 4, wherein said monomers are selected from the group consisting of styrene, butadiene, and isoprene.
6. The method of claim 1, wherein said step of polymerizing comprising the steps of:
  - providing a reaction medium;
  - adding said monomer or monomers to be polymerized to said reaction medium; and
  - adding said anionic initiator to said reaction medium.
7. The method of claim 6, wherein said reaction medium is a liquid selected from the group consisting of polar solvents, hydrocarbon solvents and mixtures thereof.
8. The method of claim 6, wherein said anionic initiator is added to said reaction medium in amounts ranging from 1 about 1000 meq/kg of said monomer.
9. The method of claim 1, further comprising the step of:
  - terminating said step of polymerizing with an agent selected from the group consisting of terminating agents, coupling agents, and linking agents to provide a functional group at the end opposite said head group.

10. The method of claim 9, wherein said terminating agents are selected from the group consisting of tin tetrachloride,  $(R)_3SnCl$ ,  $(R)_2SnCl_2$ ,  $R_4Sn$ , carbodiimides, N-cyclic amides, N,N' disubstituted cyclic ureas, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino) benzophenone, and mixtures thereof wherein R is selected from the group consisting of alkyls having from about 1 to about 20 carbon atoms, cycloalkyls having from about 3 to about 20 carbon atoms, aryls having from about 6 to about 20 carbon atoms and aralkyls having from about 7 to about 20 carbon atoms.
11. A method for anionically polymerizing monomers comprising the steps of:  
 synthesizing a sulfur containing anionic initiator *in situ*;  
 polymerizing said monomers with said sulfur containing anionic initiator to provide a functional head group on the polymer.
12. The method of claim 11, wherein said sulfur containing anionic initiator is a lithio thio aryl having the general formula



- where X is selected from the group consisting of S, O and  $NR_4$ , where R is selected from the group consisting of trimethyl-, triethyl- and tripropyl-silyl groups, C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6 to C20 aryl group and mixtures thereof; where  $n = 0$  or  $1$  and A is selected from the group consisting of phenyl, functionalized phenyls; thienyl, furyl, puridyl, naphthyl, binaphthyl, and pyrenyl; where the functionalized phenyls have the formula



where FG is selected from the group consisting of C1 to C10 alkyl groups, C2 to C10 alkenyl groups, C3 to C10 alkynyl groups, ethers, *tert*-amines, oxazolines, phosphines, sulfides, silyls, monosaccharides, sterically hindered esters and mixtures thereof.

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13. The method of claim 12, wherein said lithio thio aryl initiator is 2-lithio-2-phenyl-1,3-dithiane.
- 10 14. The method of claim 13, wherein said monomers are selected from the group consisting of conjugated dienes having from about 4 to about 12 carbon atoms and monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes and mixtures thereof.
- 15 15. The method of claim 14, wherein said monomers are selected from the group consisting of styrene, butadiene, and isoprene.
16. The method of claim 11, wherein said step of synthesizing comprises  
creating a solution of an initiator precursor and butyllithium in a solvent  
20 therefor;  
adding to said solution said monomer or monomers; and  
heating said solution for a period of time sufficient to generate said anionic initiator and polymerize said monomer or monomers.
- 25 17. The method of claim 16, wherein said initiator precursor is 2-methyl-1,3-dithiane and said anionic initiator is 2-lithio-2-methyl-1,3-dithiane.

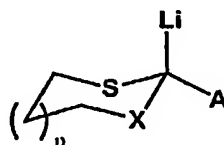
18. The method of claim 11, further comprising the step of:

terminating said step of polymerizing with an agent selected from the group consisting of terminating agents, coupling agents, and linking agents to provide a functional group at the end opposite said head group.

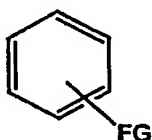
19. The method of claim 18, wherein said terminating agents are selected from the group consisting of tin tetrachloride,  $(R)_3SnCl$ ,  $(R)_2SnCl_2$ ,  $R_4Sn$ , carbodiimides, N-cyclic amides, N,N' disubstituted cyclic ureas, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino) benzophenone, and mixtures thereof wherein R is selected from the group consisting of alkyls having from about 1 to about 20 carbon atoms, cycloalkyls having from about 3 to about 20 carbon atoms, aryls having from about 6 to about 20 carbon atoms and aralkyls having from about 7 to about 20 carbon atoms.

20. A vulcanizable elastomer having reduced hysteresis properties comprising:  
a plurality of polymer molecules wherein substantially each said polymer molecule contains a functional head group derived from a sulfur containing anionic initiator; and  
from about 20 to about 100 parts by weight of carbon black, per 100 parts of said elastomer.

21. A vulcanizable elastomer according to claim 20, wherein said sulfur containing anionic initiator is a lithio thio aryl having the general formula



where X is selected from the group consisting of S, O and NR<sub>4</sub>, where R is selected from the group consisting of trimethyl-, triethyl- and tripropyl-silyl groups, C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6 to C20 aryl group and mixtures thereof; where n = 0 or 1 and A is selected from the group consisting of phenyl, functionalized phenyls; thienyl, furyl, puridyl, naphthyl; binaphthyl, and pyrenyl; where the functionalized phenyls have the formula

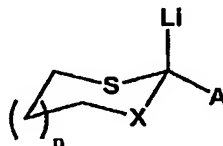


where FG is selected from the group consisting of C1 to C10 alkyl groups, C2 to C10 alkenyl groups, C3 to C10 alkynyl groups, ethers, *tert*-amines, oxazolines, phosphines, sulfides, silyls, monosaccharides, sterically hindered esters and mixtures thereof.

22. A vulcanizable elastomer according to claim 21, wherein said lithio thio aryl initiator is 2-lithio-2- phenyl-1,3-dithiane.
23. A vulcanizable elastomer according to claim 20, wherein said polymer molecules are derived from monomers selected from the group consisting of conjugated dienes having from about 4 to about 12 carbon atoms and monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes and mixtures thereof.
24. A vulcanizable elastomer according to claim 23, wherein said monomers are selected from the group consisting of styrene, butadiene, and isoprene.
25. A vulcanizable elastomer according to claim 20, wherein substantially each said polymer molecule contains a functional terminal group derived from an agent

selected from the group consisting of terminating agents, coupling agents, and linking agents.

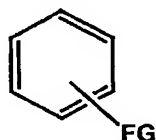
26. A vulcanizable elastomer according to 25, wherein said terminating agents are  
 5 selected from the group consisting of tin tetrachloride,  $(R)_3SnCl$ ,  $(R)_2SnCl_2$ ,  $R_4Sn$ , carbodiimides, N-cyclic amides, N,N' disubstituted cyclic ureas, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino) benzophenone, and mixtures thereof wherein R is selected from the group consisting of alkyls having from about 1 to about 20 carbon atoms, cycloalkyls  
 10 having from about 3 to about 20 carbon atoms, aryls having from about 6 to about 20 carbon atoms and aralkyls having from about 7 to about 20 carbon atoms.
27. An improved tire having decreased rolling resistance resulting from a  
 15 treadstock containing a vulcanizable elastomer compound comprising:  
     an elastomer comprising a plurality of polymer molecules wherein substantially each said polymer molecule contains a functional head group derived from a sulfur containing anionic initiator; and  
     from about 20 to about 100 parts by weight of carbon black, per 100  
 20 parts of said elastomer.
28. An improved tire according to claim 27, wherein said sulfur containing anionic initiator is a lithio thio aryl having the general formula



- 25 where X is selected from the group consisting of S, O and  $NR_4$ , where R is selected from the group consisting of trimethyl-, triethyl- and tripropyl-silyl



groups, C1 to C20 alkyl groups, C4 to C20 cycloalkyl groups, C6 to C20 aryl group and mixtures thereof; where  $n = 0$  or  $1$  and A is selected from the group consisting of phenyl, functionalized phenyls; thienyl, furyl, puridyl, naphthyl, binaphthyl, and pyrenyl; where the functionalized phenyls have the formula



5

where FG is selected from the group consisting of C1 to C10 alkyl groups, C2 to C10 alkenyl groups, C3 to C10 alkynyl groups, ethers, *tert*-amines, oxazolines, phosphines, sulfides, silyls, monosaccharides, sterically hindered esters and mixtures thereof.

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29. An improved tire according to claim 28, wherein said lithio thio aryl initiator is 2-lithio-2-phenyl-1,3-dithiane.
30. An improved tire according to claim 27, wherein said polymer molecules are derived from monomers selected from the group consisting of conjugated dienes having from about 4 to about 12 carbon atoms and monovinyl aromatic monomers having 8 to 18 carbon atoms and trienes and mixtures thereof.
31. An improved tire according to claim 30, wherein said monomers are selected from the group consisting of styrene, butadiene, and isoprene.
32. An improved tire according to claim 27, wherein substantially each said polymer molecule contains a functional terminal group derived from an agent selected from the group consisting of terminating agents, coupling agents, and linking agents.

25

- 5 33. An improved tire according to 32, wherein said terminating agents are selected from the group consisting of tin tetrachloride,  $(R)_3SnCl$ ,  $(R)_2SnCl_2$ ,  $RSnCl_3$ , carbodiimides, N-cyclic amides, N,N' disubstituted cyclic ureas, cyclic amides, cyclic ureas, isocyanates, Schiff bases, 4,4'-bis(diethylamino) benzophenone, and mixtures thereof wherein R is selected from the group consisting of alkyls having from about 1 to about 20 carbon atoms, cycloalkyls having from about 3 to about 20 carbon atoms, aryls having from about 6 to about 20 carbon atoms and aralkyls having from about 7 to about 20 carbon atoms.

**ABSTRACT OF THE DISCLOSURE**

A method is presented for anionically polymerizing monomers comprising the step of polymerizing the monomers with a sulfur containing anionic initiator to provide a functional head group on the polymer. Another method provides for anionically polymerizing monomers comprising the steps of synthesizing a sulfur containing anionic initiator *in situ* and polymerizing the monomers with the sulfur containing anionic initiator to provide a functional head group on the polymer. A vulcanizable elastomer having reduced hysteresis properties comprises a plurality of polymer molecules wherein substantially each polymer molecule contains a functional head group derived from a sulfur containing anionic initiator; and from about 20 to about 100 parts by weight of carbon black, per 100 parts of the elastomer. An improved tire having decreased rolling resistance resulting from a treadstock containing a vulcanizable elastomer compound comprises an elastomer comprising a plurality of polymer molecules wherein substantially each polymer molecule contains a functional head group derived from a sulfur containing anionic initiator; and from about 20 to about 100 parts by weight of carbon black, per 100 parts of the elastomer.

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